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Melt Modification of Poly(styrene-*co*-maleic anhydride) with Alcohols in the Presence of 1,3-Oxazolines

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ABSTRACT: Various copolyesteramides were prepared by melt compounding at 220 °C involving reaction of poly(styrene-*co*-maleic anhydride), SMA, with 6, 17, and 28 wt % maleic anhydride content, and 1-dodecanol, *C12OH*, in the presence of 2-undecyl-1,3-oxazoline, *C11OXA*. Copolymer architectures were examined by means of ¹H NMR, FTIR, DSC, and TGA using model compounds prepared via solution reactions. While conversion of anhydride with alcohol was poor due to the thermodynamically favored anhydride ring formation, very high conversions were achieved when stoichiometric amounts of *C11OXA* were added. According to spectroscopic studies esteramide groups resulted from reaction of oxazoline with carboxylic acid intermediate. In the absence of alcohol, *C11OXA* reacted with anhydride to produce esterimides. Effective attachment of flexible *n*-alkyl side chains via simultaneous reaction of *C12OH* and *C11OXA* resulted in lower glass-transition temperatures of copolyesteramides. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 1222–1231, 2000

Keywords: poly(styrene-*co*-maleic anhydride); oxazoline; alcohol; reactive processing; melt reaction

INTRODUCTION

Poly(styrene-*co*-maleic anhydride), SMA, can easily be modified by polymer analogous reaction via addition of low molecular weight compounds, for example, water, alcohols, or amines, because of high reactivity of the anhydride group of SMA. The hydrolysis of SMA results in poly(carboxylic acids), which are widely used in the paper industry as polymeric binder. Also partially hydrolyzed SMA can be used as pigment dispersant for aqueous paints and inks. However, the poor solubility of hydrolyzed SMA in nonpolar solvents excludes its applications in hydrophobic media of coatings, additives and paints as well as powder applica-

tion or plastic additives. Therefore, SMA is modified by reaction with fatty alcohols, thus increasing its solubility in organic solvents.^{1,2} SMA and SMA derivatives are well known compatibilizers for polymer blends.^{3–8}

The modification of SMA with aliphatic alcohols is shown in Figure 1 (pathway a). The extent of anhydride conversion depends strongly on temperature. At high temperatures, reversible hemiesterification is shifted back to the educt side, thus accounting for poor anhydride conversion.^{9–12} In order to overcome the problem of limited anhydride conversion, solution processes use large molar excess of alcohol. Melt modification of SMA is even less effective because temperatures above *T_g* of SMA are required, thus shifting the chemical equilibrium further towards the educt side. According to Lambla's detailed study on this reversible esterification reaction, hemi-esters of

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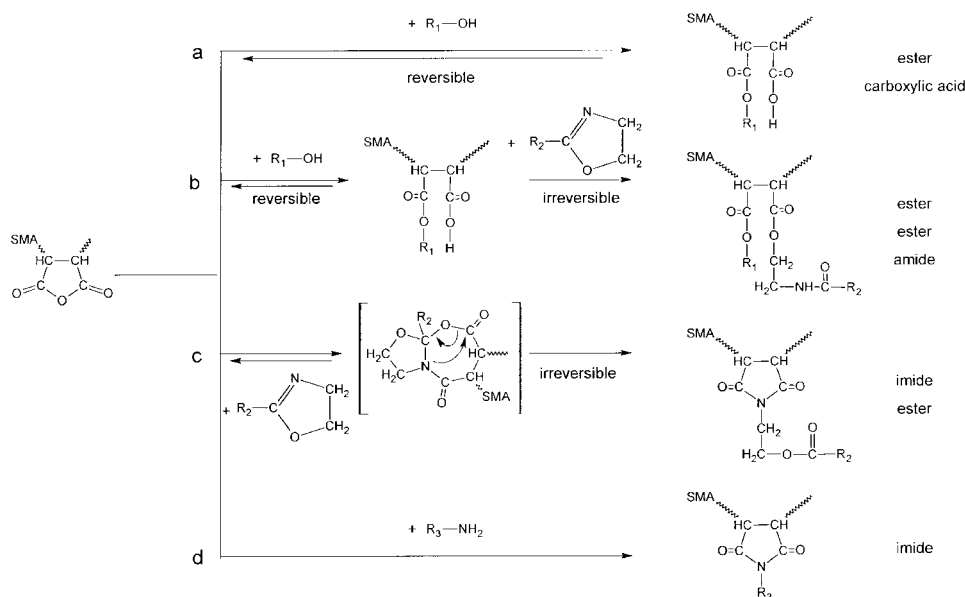


Figure 1. Reaction of SMA with alcohols and oxazolines: reversible ester formation of ester carboxylic acids (pathway a), irreversible formation of ester-ester amides (pathway b), and irreversible ester imide formation (pathway c). Reaction of SMA with amines: irreversible imide formation (pathway d).

alcohols with long alkyl substituents are more stable than with short alkyl substituents because of sterical hindrance of ester hydrolysis.¹² However, melt reaction of SMA with alcohols fails to achieve high anhydride conversion. Quantitative anhydride conversion is only known for the reaction of SMA with primary amines as shown in Figure 1 (pathway d).¹³⁻¹⁵ In contrast to reversible ester formation, the irreversible imide formation leads to quantitative conversion both in solution and in melt.

In order to afford high conversion with alcohols, it is important to shift the equilibrium of esterification to the product side by removing the *in situ* generated carboxylic acid from the system by a subsequent reaction. For example, 1,3-oxazolines are well known to afford quantitative conversion of carboxylic acids both in melt and in solution processes.¹⁶ Because of their high reactivity, oxazolines are especially suitable for polymer analogous reactions in polymer melts. This solvent-free addition reaction yields ester amides quantitatively without formation of any by-products.^{17,18} Consequently, 1,3-oxazolines are suitable compounds that are capable of effectively trapping the carboxylic acids in melt as depicted in Figure 1 (pathway b).

However, it has been shown that 1,3-oxazolines can also react with anhydrides in the absence of

alcohol via zwitterionic polymerization as depicted in Figure 2 (pathway a). For example, Rowland has claimed an alternative mechanism, that is, the formation of an ester imide for the reaction of succinic anhydride and 2-methyloxazoline shown in Figure 2 (pathway b). Also Kobayashi sug-

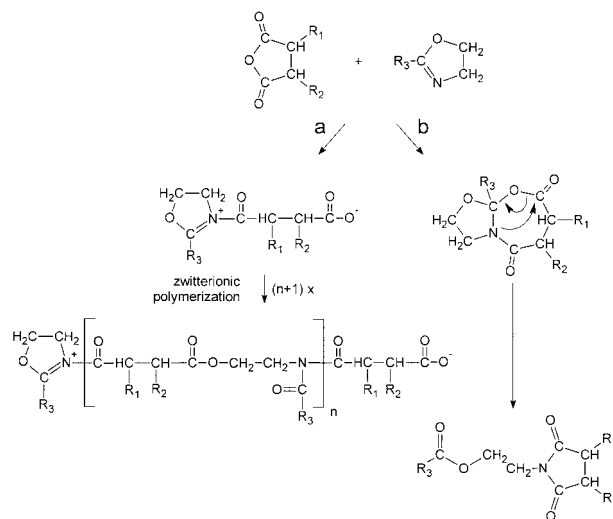


Figure 2. Reaction mechanism of 1,3-oxazolines with cyclic dicarboxylic acid anhydrides: polymerization via zwitterionic intermediates (pathway a) and ester imide formation via bicyclic intermediates (pathway b).

gested that the reaction of 1,3-oxazolines with cyclic anhydrides involves the formation of a bicyclic species, which undergoes a rearrangement in order to give the more stable ester imide as shown in Figure 2 (pathway b).¹⁹ For the polymer analogous reaction of SMA with 1,3-oxazolines, a mechanism involving bicyclic species was first considered by Lee et al.²⁰ However, the reaction was only performed in DMSO solution at 80 °C. Mäder et al. have used SMA recently as reactive compatibilizer in melt at high temperatures.²¹ Oxazoline-functional polymers could be compatibilized reactively with SMA taking advantage of the high reactivity of the anhydride/oxazoline system. Recently, Schmidt–Naake observed esterimide formation by the melt-reaction of 1,3-oxazoline-functional SAN with phthalic anhydride.²²

Poe et al. were the first to find that in a ternary system consisting of anhydride, 1,3-oxazoline, and alcohol the hemi-esterification between anhydride and alcohol is preferred with respect to the reaction of anhydride and oxazoline. Subsequently, the *in situ* generated carboxylic acid reacts with 1,3-oxazoline yielding poly(esteramide)s as shown in Figure 1 (pathway b).^{23,24} Additionally, we have shown that in such a ternary system imide formation can occur as a minor side reaction, thus reducing molecular weight.²⁵

The aim of this study was to demonstrate that 1,3-oxazolines are suitable low molecular weight compounds able to promote solvent-free melt modification of SMA with alcohols and to achieve high anhydride conversion by reactive processing technology. Furthermore, the potential of 1,3-oxazolines as sole melt modifier for SMA in the absence of any alcohol was examined in order to clarify the role of cross-linking via zwitterionic species.

EXPERIMENTAL

Materials

2-Undecyl-4,5-dihydro-1,3-oxazoline, *C11OXA*, was supplied from Henkel AG and distilled prior to use. 1-Octanol, *C8OH*, and 1-dodecanol, *C12OH*, were purchased from Aldrich and purified by distillation. 2-(9-Decen-1-yl)-1,3-oxazoline, *C10enOXA*, was synthesized according to literature procedure.²⁶ The poly(styrene-co-maleic anhydride), SMA, was supplied by DSM and BASF as granulate and dried at 60 °C in vacuum for 24 h. The maleic anhydride, MA, content was 6, 17, and 28

wt %. Ethylbenzene p.a., EtBz, was purchased by Aldrich and used as received.

Solution Reaction

1 g SMA17 was dissolved in 6.54 mL EtBz, that is, the anhydride concentration was 0.266 mol/L (10 wt %). After addition of *C8OH* and/or *C11OXA* the solution was heated under reflux for 2 h. In order to analyze the conversion after different time periods, samples were taken using a syringe. The products were precipitated in ice-cooled methanol, dissolved in THF and again precipitated in ice-cooled methanol.

Melt Reaction

The melt reactions were performed in a DACA twin-screw microcompounder at 220 °C and 100 rpm. The mixing chamber had a total volume of 5 mL and was charged with about 2 mL SMA. Then *C12OH* and *C11OXA* were added. The remaining SMA was filled into the mixing chamber ($t = 0$). This procedure guaranteed that the low molecular weight reactants and the SMA were mixed quickly in the compounder. Torque and normal force were recorded every minute. After 9 min the reaction product was quickly recovered and dissolved in THF and precipitated in ice-cooled methanol twice.

Characterization

Differential Scanning Calorimetry (DSC). Glass transition temperatures (T_g) were recorded with a Perkin–Elmer DSC-7 using a heating rate of 10 K/min (second heating run).

Thermo Gravimetric Analysis (TGA). Thermogravimetric analysis was performed on a Netzsch STA 409. The samples were heated under nitrogen atmosphere applying a heating rate of 10 K/min.

Nuclear Magnetic Resonance Spectroscopy (NMR). The ¹H NMR spectra were recorded in CDCl₃ on a Bruker ARX-300 at 300 MHz. TMS was utilized as internal standard.

Fourier Transformed-Infrared Spectroscopy (FTIR). The FTIR spectra were recorded on a Bruker IFS 88 spectrometer with MIR-DTGS detector and KRS-5 polarizer. Thin films were

Table I. Solution Reaction at 138 °C ($t = 120$ min) of SMA17 with *C12OH* and *C11OXA* at Different Stoichiometric Ratios and Measured Anhydride Conversion

Sample	Stoichiometric Factor ^a		Anhydride Conversion [%] FTIR ^b
	<i>C8OH</i>	<i>C11OXA</i>	
SMA17	—	—	0
S17A1	1	0	7
S17A8	8	0	73
S17A101	1	1	30
S17A202	2	2	78
S17A801	8	1	74
S17A8Oen1 ^c	8	1 ^c	76

^a Concentration of alcohol and oxazoline relative to anhydride concentration.

^b Relative decrease of IR signal at 1780 cm^{-1} (anhydride vibration) in comparison to SMA17.

^c *C10enOXA* was used.

prepared on KBr pellets by evaporation of a THF solution of the respective polymers.

RESULTS AND DISCUSSION

Solution Reaction

In the first step, the solution reaction of SMA17 with 1-octanol (*C8OH*) and the mixture of *C8OH* with 2-undecyl-1,3-oxazoline (*C11OXA*) is studied. *C8OH* and *C11OXA* are added stoichiometrically or excess with stoichiometric ratios as listed in Table I. All samples in this investigation are termed $SxAyOz$, where S = SMA, A = alcohol compound, and O = oxazoline compound. The number x denotes the anhydride content (wt %) in the SMA and the numbers y and z give the stoichiometric ratios of added alcohol (y) and oxazoline (z) compound with respect to the anhydride. As discussed in more detail below, *C11OXA* is replaced by *C10enOXA* in the sample S17A8Oen1.

All precipitated polymers are white powders and soluble, thus indicating that no crosslinking is observed. Figure 3 shows the FTIR spectra of *C11OXA*, SMA17, S17A8, and S17A202 from 1400 to 2000 cm^{-1} . For better illustrations only the significant functional groups are graphically assigned to the corresponding signals. The spectra are normalized with respect to the polymer film thickness on the KBr pellet using the SMA

backbone phenyl vibration signal at 1494 cm^{-1} as internal reference. In order to quantify the anhydride conversion, the corresponding FTIR signals are integrated.⁹ In further discussion, the signals are termed corresponding to functional group + wavenumber in cm^{-1} . For example, ANH1780 names the anhydride signal at 1780 cm^{-1} . Table II summarizes the assignments of FTIR signals and the integration range used for quantitative evaluation.

The FTIR spectrum of *C11OXA* shows the typical oxazoline C=N vibration OXA1664. SMA17 exhibits the two characteristic signals of the anhydride ANH1860 and ANH1780 and the phenyl ring (Ref1494). For both S17A8 and S17A202 the anhydride signals ANH1860 and ANH1780 are decreased, indicating almost complete anhydride conversion. S17A8 shows an additional strong signal CO1708, which is assigned to the carbonyl vibration of a carboxylic acid and a strong signal CO1732 corresponding to the ester carbonyl vibration. These observations are in accordance with the well-known formation of a hemi-ester carboxylic acid shown in Figure 1 (pathway a). S17A202 shows the new signals CO1732, CO1677, and AMIDE1533. After a reaction time of 120 min no signal CO1708 of carboxylic acids is detectable.

In order to detect intermediate carboxylic acid, samples of S17A8Oen1 are recovered during so-

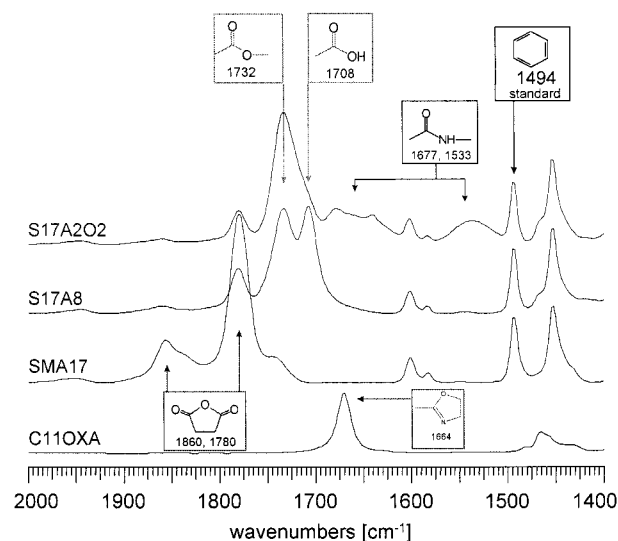
**Figure 3.** FTIR spectra of *C11OXA*, SMA17, S17A8 (SMA17 modified with *C8OH* in solution), and S17A202 (SMA17 modified with *C8OH* and *C11OXA* in solution). Arrows indicate the assignment of the signals to the functional groups.

Table II. FTIR Signals of Functional Groups and Assigned Frequency Range for Quantitative Evaluation

Functional Group	Abbreviation	Wave Numbers [cm ⁻¹]	Range for Integration [cm ⁻¹]
Aliphatic proton	CH2900	2900	2985–2802
Anhydride 1	ANH1860	1860	1917–1817
Anhydride 2	ANH1780	1780	1817–1757
Imide 1	IMIDE1772	1772	— ^a
Imide 2	IMIDE1699	1699	— ^a
Ester	CO1732	1732	1757–1690
Carboxylic acid	CO1712	1712	— ^a
Amide 1	CO1677	1677	1690–1617
Oxazoline	OXA1664	1664	— ^a
Amide 2	AMIDE1533	1533	1572–1506
Phenyl (standard)	Ref1494	1494	1506–1480
Anhydride 3	ANH1067	1067	1120–1041

^a Signals were not integrated quantitatively.

lution reaction. The time-dependent conversion is monitored via the decreasing anhydride signals ANH1860 and ANH1780. Simultaneously, the ester signal CO1732 increases with increasing reaction time. During the first 30 min, this ester signal, CO1732, is accompanied by a smaller signal, CO1712, which is attributed to correspond to *in situ* generated carboxylic acid. After 60 min CO1712 is only visible as a small shoulder of the strong CO1732 band. As described above, CO1712 disappears completely after 120 min. Overall, the kinetic FTIR investigation confirms ester–ester amide formation via *in situ* generated carboxylic acids as shown in Figure 1 (pathway b). Consequently, C11OXA addition converted free carboxylic acid.

In order to quantify the anhydride conversion, the ANH1780 signal of the products is compared with the ANH1780 signal of the educt SMA17. For the binary system, S17A1, an anhydride conversion of only 7% is observed. As expected an 8-fold excess of C8OH (S17A8) gives much a higher anhydride conversion of 73%. Addition of oxazoline to the SMA/alcohol mixture also increases anhydride conversion. For example, S17A1O1 exhibits an anhydride conversion, which is 5 times higher than that of S17A1. The highest anhydride conversion, however, is observed by 2-fold excess of C8OH and C11OXA. In conclusion, in the presence of oxazoline, which acts as a carboxylic acid scavenger, much higher anhydride conversions are achieved at much lower alcohol content with respect to hemi-ester formation of the binary an-

hydride/alcohol system. High anhydride conversion is already achievable at reduced alcohol concentration via oxazoline addition.

In order to distinguish between grafted alcohol and grafted oxazoline, SMA is modified with C8OH and C10enOXA (sample S17A8Oen1). According to Figure 1 (pathway b) such modified SMA contains both unsaturated side chains, resulting from grafted C10enOXA, and aliphatic side chains, resulting from grafted C8OH. These signals can be easily analyzed separately by means of ¹H NMR. Figure 4 displays the ¹H NMR spectra of the educts C10enOXA, C8OH, and SMA17 and the resulting product S17A8Oen1. In this section only the signals relevant for grafting

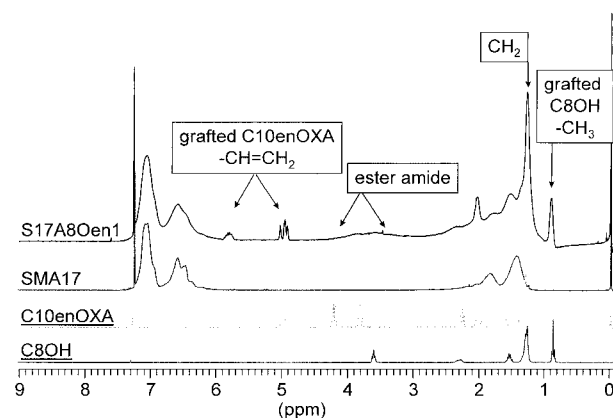


Figure 4. ¹H NMR spectra of C8OH, C10enOXA, SMA17, and S17A8Oen1 (SMA17 solution modified with C8OH and C10enOXA).

Table III. Melt Reaction at 220 °C ($t = 9$ min) of SMA with *C12OH* and *C11OXA*: Glass-Transition Temperature and Anhydride Conversion

Sample	Stoichiometric Factor ^a		T_g^b [°C]	Conversion of Anhydride ^c
	<i>C12OH</i>	<i>C11OXA</i>		
SMA6	—	—	113	—
S6A1	1	0	109	10
S6A1O1	1	1	81	74
S6O1 ^d	0	1	96	44 ^d
SMA17	—	—	136	—
S17A1	1	0	120	14
S17A1O1	1	1	62	66
S17O1 ^d	0	1	77	59 ^d
SMA28	—	—	158	—
S28A1	1	0	142 ^e	25
S28A1O1	1	1	50 ^e	67
S28O1 ^d	0	1	81	73 ^d

^a Concentration of alcohol and oxazoline relative to anhydride concentration.

^b Measured at 10 K/min (second heating).

^c Relative decrease of IR signals ANH1780 in comparison to SMA educt.

^d Relative decrease of IR signals ANH1860 in comparison to SMA educt.

^e Hardly detectable (very broad).

reaction will be discussed. *C10enOXA* shows the typical methylene triplets of the oxazoline ring at 3.8 and 4.2 ppm, and the olefinic hydrogens give signals at 5.0 and 5.8 ppm. Additionally, the long methylene chain has an intense signal at 1.2 ppm. *C8OH* gives a methylene signal at 3.6 ppm and a CH_3 signal at 0.9 ppm. The copolymer SMA17 shows only two very broad signals at 1.1–2.4 (aliphatic hydrogens) and 6.1–7.3 ppm (aromatic hydrogens), which will not be discussed further in detail. Unfortunately, the hydrogens of the anhydride ring structure are not detectable as a separate signal in the ^1H NMR spectrum.

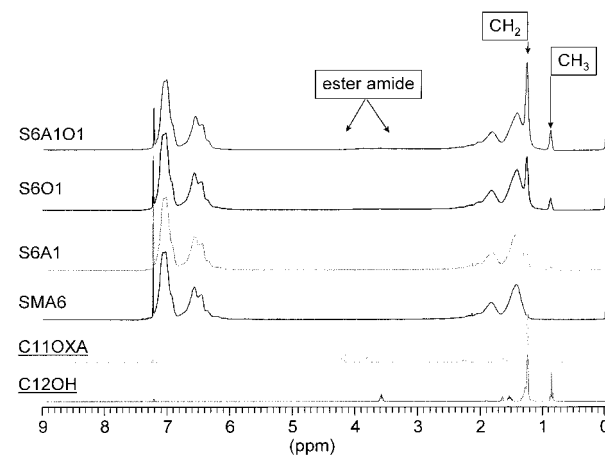
In the ^1H NMR of the product S17A8Oen1, the broad signals of the aliphatic hydrogens are now accompanied by new signals at 0.9, 1.2, and 2.1 ppm, which correspond to grafted alkyl side chains. In the range from 2.8 to 4.3 ppm a new broad signal is visible. This is attributed to covalent grafting, that is, the methylene groups in the vicinity of the ester arising from grafted *C8OH* and the methylene groups in the vicinity of the ester–amide arising from grafted *C10enOXA*. The broadness of this signal is explained by the re-

duced mobility of these methylene groups close to the SMA17 backbone. Unfortunately, these signals do not prove explicitly the ester–ester amide structure according Figure 1 (pathway b). However, S17A8Oen1 does also show olefinic signals at 5.0 and 5.8 ppm arising from grafted *C10enOXA*. These olefinic signals arise exclusively from grafted *C10enOXA*, whereas the methyl signal at 0.9 ppm corresponds exclusively to grafted *C8OH*. Thus, ^1H NMR can distinguish between grafted *C8OH* and *C10enOXA*. The molar ratio of grafted *C8OH* and *C10enOXA* is close to 1 as determined by integration of the respective signals. This proves that solution reaction of SMA with *C8OH* and *C11OXA* yields side-chain-grafted products containing approximately equimolar amounts of both compounds.

These spectroscopic observations provide strong experimental evidence that the reaction of SMA with alcohols and 1,3-oxazolines yields exclusively ester–ester amides, resulting from quantitative conversion of the *in situ* formed carboxylic acid with oxazoline. The competing reaction of oxazoline with anhydride, which would lead to crosslinking of the SMA backbone, is not reflected by spectroscopic measurements. The solubility of S17A1O1 indicates that formation of zwitterionic crosslinks can be neglected.²⁷ Further analysis of the mechanism requires detailed kinetic studies.

Melt Reaction

Table III summarizes the physical properties of the samples prepared by melt modification of

**Figure 5.** ^1H NMR spectra of *C12OH*, *C11OXA*, SMA6, and SMA6 modified in melt: S6A1 with *C12OH*, S6O1 with *C11OXA*, and S6A1O1 with both *C12OH* and *C11OXA*.

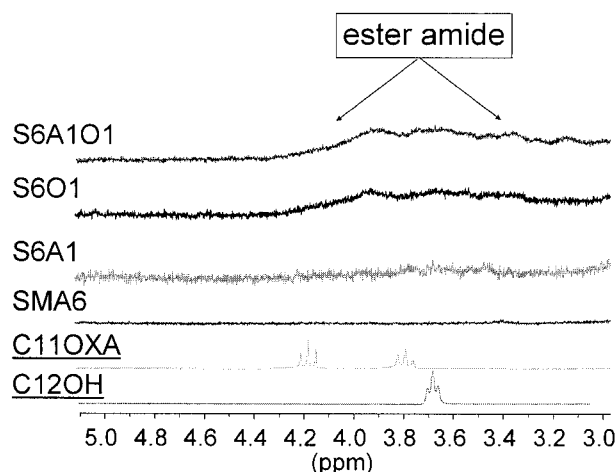


Figure 6. Enlarged ester amide section of ^1H NMR spectra of Figure 5.

SMA with MA content of 6, 17, and 28 wt %, respectively. All received polymers are transparent and their color is pale yellow to yellow (color formation increases with increasing oxazoline content). For S28O1 a small amount of gas formation is observed as reflected by the presence of small gas bubbles.

After a reaction time of 9 min, the samples S6O1 and S6A1 are investigated by means of ^1H NMR without purification. As expected residual *C12OH* (3.66 ppm, $\text{CH}_2\text{—O}$) and *C11OXA* (3.78, 4.18 ppm, $\text{N—CH}_2\text{—CH}_2\text{—O}$) are detectable. ^1H NMR spectra of *C12OH*, *C11OXA*, SMA6, and purified S6A x O y samples are depicted in Figure 5. The educt signals disappear completely after purification. The SMA6 educt shows two very broad signals as discussed in detail for SMA17 in the previous section. The signals from 6.1 to 6.8 ppm are used for normalization of the product spectrum. The signal of the methyl group of grafted *C12OH* and/or *C11OXA* is clearly visible as a distinct signal at 0.8 ppm. The methylene groups of grafted *C12OH* and/or *C11OXA* appear at 1.2 ppm. The expected signals for the methylene groups vicinal to the ester (resulting from grafted *C12OH*) and/or ester amide (resulting from grafted *C11OXA*) are very broad due to reduced mobility in the vicinity of the polymer backbone as shown in the enlarged product spectra in Figure 6 (3 to 5 ppm). The comparison of ^1H NMR spectra of melt modified products and solution model compounds shows no significant differences. The amount of grafted side chains increases in the order $\text{S6A1} < \text{S6O1} < \text{S6A1O1}$, as can be seen from the increasing methyl signal at

0.9 ppm. Quantitative analysis of the grafting reaction is achieved by means of FTIR spectroscopy.

The FTIR signals of SMA melt modified with alcohol (SxA1) or with both alcohol/oxazoline mixtures (SxA1O1) are the same as discussed above for the corresponding solution reactions. This proves that melt reaction of SMA at 220 °C yields the same products as the solution reaction at 138 °C. No intermediate carboxylic acid is detectable when oxazoline is added. This again proves the high efficiency of *C11OXA* as a trapping agent for carboxylic acids in the melt and is attributed to the high reactivity of oxazolines at 220 °C.²⁵

The anhydride conversion of samples SxA1 and SxA1O1 is determined as described for the solution process. Unfortunately, this is impossible for samples that are modified exclusively with *C11OXA* (SxO1) because of differences of their FTIR spectra. A signal at 1772 cm^{-1} with a similar intensity in comparison to the adjacent signal ANH1780 of pure SMA is observed. Because of the close proximity of ANH1780 and the signal at 1772 cm^{-1} , it is assigned to the remaining anhydride. However, the second anhydride signal, ANH1860, decreases. This indicates that the anhydride has reacted and the product corresponds to the signal at 1772 cm^{-1} . New signals are observed at 1699, 1732, 1677, and 1533 cm^{-1} . The strong imide signals IMIDE1772, IMIDE1699, and the ester signal CO1732 correspond to the formation of the ester imide displayed in Figure 2 (pathway b). However, the weak amide signals CO1677 and AMIDE1533 indicate the presence of a small amount of amide formation, which could correspond to zwitterion formation as displayed in Figure 2 (pathway a). As described above, the signal ANH1780 does not decrease for the binary system because of imide formation. Therefore, ANH1860 is used for quantitative evaluation of SxO1 instead of ANH1780. Table III lists the determined anhydride conversion of all samples. Schmidt and coworkers have investigated the melt reaction of SMA16 and SMA32 with *C12OH* using a 2-fold excess of alcohol.² At 200 °C the same equilibrium anhydride conversion of 57% was reached within 5 and 30 min for SMA32 and SMA16, respectively. Here, we want to show that anhydride conversion can be improved by oxazoline addition. Thus, we chose reaction conditions at $T = 220\text{ °C}$ where the reaction velocity is very high, enabling reactive melt processing. The high temperature causes shifting of the equilibrium conversion to the educt side. This allows us to

prove the merit of oxazoline addition to increase the maximum achievable conversion in the melt.

The equilibrium conversion is reached within 9 min for the binary system S6A1 comprising of SMA6 and *C12OH*. As expected, all binary systems exhibit only low conversion due to thermodynamic control at 220 °C. The relative anhydride conversion increases from 10 to 14 and 25% in the order S6A1, S17A1, and S28A1. Most likely this effect can be attributed to the catalytic effect of carboxylic acids of the formed hemi-ester, which catalyze further esterification during the time elapsing when the reaction products cool down to ambient temperature.² At lower temperatures the chemical equilibrium is shifted towards the product side. Addition of *C11OXA*, that is, ternary systems S6A1O1, S17A1O1, and S28A1O1, yields much higher conversion compared to that of the corresponding binary systems. In all cases an anhydride conversion of about 70% is observed under identical reaction conditions. This proves that addition of *C11OXA* as trapping agent is very effective in melt.

Another important question is the reaction of 1,3-oxazoline with anhydride in the absence of alcohols. In all cases anhydride conversion of the binary oxazoline/anhydride system is significantly higher for the oxazoline modified SMA than for the respective alcohol modified SMA. The conversion of anhydride increases from 44 over 59 to 73% in the order S6O1 < S17O1 < S28O1. The absence of cross-linking in the system SMA/*C11OXA* supports again the previous finding that the dominating reaction mechanism is the ester imide formation instead of the zwitterionic polymerization. This proves that melt modification of SMA is possible with *C11OXA* instead of *C12OH*.

Thermal Characterization

Grafting of highly flexible *n*-alkyl side chains has a strong impact on flexibility of the SMA backbone. Consequently, the glass-transition temperature, T_g , should decrease with increasing amount of grafted *n*-alkyl side chains. At the same time, the chemical structure of the SMA backbone is significantly changed, that is, the 5-membered anhydride ring is converted either into (a) an ester carboxylic acid, (b) an ester ester, or (c) an imide (Fig. 1). These different chemical structures may lead to different thermostabilities. In order to examine structure/property correlation, the modified samples are investigated by means of differential scanning calorimetry, DSC,

and thermo gravimetric analysis, TGA. The T_g of all melt-modified samples and corresponding SMA educts are listed in Table III. As expected the T_g of SMA educts increases from 113 over 136 to 158 °C with increasing MA content for SMA6, SMA17, and SMA28.²⁸ All modified samples exhibit low T_g ranging from 77 to 140 °C. This is caused by the flexible *n*-alkyl side chains and the change of the backbone structure. At constant MA content T_g decreases in the order $SMA_x > SxAl > SxO1 > SxO1A1$ for all investigated MA contents $x = 6, 17$, and 28 wt % as a consequence of increasing amount of grafted *n*-alkyl side chains. The SMA samples modified with *C12OH*, that is, $SxA1$, show slightly reduced T_g because of a low amount of grafting. As expected, T_g is reduced strongly for $SxO1$ samples, as the melt reaction with *C11OXA* affords much more grafting with respect to *C12OH*. Samples $SxA1O1$, representing products from melt modification of SMA with *C12OH* and *C11OXA*, show the lowest T_g because of high anhydride conversion and "double grafting" per anhydride group, that is, covalent bond formation to alcohol and oxazoline groups. For example, S28A1O1 shows the largest reduction of T_g from 158 to 50 °C because of the highest amount of grafted alkyl side chains.

Figure 7 displays the first derivatives of TGA traces of SMA28 and melt modified samples. Pure SMA28 decomposes in a single step at 384 °C. This is in contrast to literature where another second decomposition step is reported at 550 °C because of decomposition of anhydride.²⁹ The melt modified samples exhibit two decomposition processes. The first decomposition step at 280 °C can be attributed to residual educts *C11OXA* and *C12OH*. The TGA trace of S28A1 resembles that of pure SMA28. The main decomposition occurs at 378 °C resulting from decomposition of the backbone, consisting mainly of unreacted SMA28 and small amount of ester carboxylic acid. For S28A1O1 the decomposition is detected at 384 °C. Obviously, its ester-ester amide structure has a thermostability similar to SMA28. In contrast S28O1 shows its second decomposition step at 394 °C, which is 16 °C higher than that of SMA28. This better thermostability implies that the chemical structure of S28O1 is different from the chemical structure of the previous systems. According to FTIR analysis, imide formation accounts for this higher thermostability of S28O1 in comparison to that of pure SMA28. In order to support this hypothesis, a model imide is prepared by melt modification of SMA28 with 1-do-

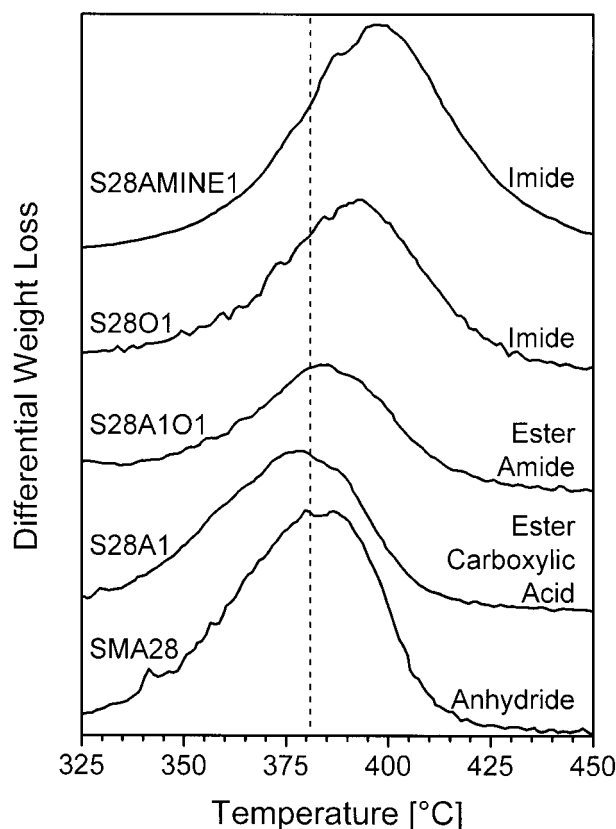


Figure 7. Differential thermo gravimetric analysis of SMA28 and melt-modified samples. Assigned chemical structure of the SMA backbone is given on the right side.

decylamine as shown in Figure 1 (pathway d). The FTIR signals IMIDE1772 and IMIDE1699 confirm imide formation. As expected, the model imide S28AMINE1 decomposes at $T = 396$ °C, that is, 18 °C higher than SMA28. Overall increased thermostability of solely oxazoline modified SMA28, that is, S28O1, indicates once more the proposed imide structure.

SUMMARY AND CONCLUSIONS

Poly(styrene-co-maleic anhydride), SMA, was successfully modified in solution and in melt using alcohol, oxazoline, or alcohol/oxazoline mixtures. Reactions in EtBz solution at 138 °C have been performed in order to obtain model graft copolymers for spectroscopic comparison. In solution, the addition of C11OXA improves anhydride conversion from about 15% for the system SMA/C12OH to about 70% for the system SMA/C12OH

+ C11OXA. Long reaction time of 2 h and large excess of C8OH and C11OXA are required to obtain high anhydride conversion. Kinetic studies by means of FTIR and ^1H NMR support a two-step reaction pathway. In the first step the well known reversible reaction of alcohol and anhydride forms an ester carboxylic acid. Subsequently, this *in situ* generated carboxylic acid and oxazoline react to form an ester amide in an irreversible reaction.

Melt reaction of SMA with C12OH added stoichiometrically affords even lower anhydride conversion of about 10%, because high melt temperatures shift the chemical equilibrium towards the educt side. Similar to solution processes, addition of C11OXA as trapping agent for *in situ* generated carboxylic acid produces high anhydride conversion. At 220 °C a maximum anhydride conversion of 70% is reached within much shorter reaction time of only 9 min.

The use of single C11OXA for melt modifying of SMA yields soluble products with high anhydride conversion. This is attributed to the high oxazoline/anhydride reactivity in combination with the irreversible formation of an ester imide. Contrary to findings for reactions of low molecular weight anhydrides at lower temperatures^{30–39} no zwitterionic polymerization is observed that would favor crosslinking and prohibit melt processing. Both spectroscopic observation and thermal properties indicate effective grafting of side chains via ester imide bond formation. The resulting graft copolymers exhibit T_g below pure SMA in the range from 50 to 160 °C. Glass temperature decrease correlates with an increasing amount of grafted *n*-alkyl side chains on the SMA backbone.

Addition of oxazoline to the system SMA/alcohol improves the anhydride conversion and enables fast reactive melt processing in the absence of any solvent. Furthermore, the system SMA/oxazoline yields novel side-chain-grafted products with high anhydride conversion. The addition of an oxazoline component avoids uneconomic high excess of a grafting reagent as known for the system SMA/alcohol, where high anhydride conversion requires high alcohol excess. However, the quantitative conversion of the system anhydride/amine cannot be reached. Furthermore, the melt modification of SMA with alcohol and oxazoline leads to new physical properties different in T_g , thermostability, and hydrophilicity.¹

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